

ESCA AND FTIR STUDIES OF BITUMINOUS COAL

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ABSTRACT

Bituminous coal from the Illinois #6, Upper Freeport, Pittsburgh and Kentucky #9 seams were examined by Electron Spectroscopy for Chemical Analysis (ESCA) and Fourier Transform Infrared Spectroscopy (FTIR). These coals were stored under various conditions (air, N_2 , mine water) and received in forms progressing from raw to ash - removed coal, (raw, milled, processed). ESCA was utilized to determine surface elemental composition and functional groups with particular attention given to C, O, N and S. Sulfur and oxidized coal models have been examined to determine the sulfur and carbon species present at the surface. FTIR has been used to correlate functional group assignments with the ESCA results.

INTRODUCTION

The surface composition characteristics of coal are important to the behavior of coal in various processing techniques. This study focuses on the surface of coal in powder form, with emphasis on the elemental composition of the surface of coal, and the functionality of C, O, N and S. One interesting application of this information would be to study the wettability of coal, of concern in agglomeration in various cleaning processes. Agglomerated coal could be separated from mineral matter.(1,2)

Both ESCA and FTIR were used in the study of four bituminous coals. These coals were taken from the Illinois #6, Kentucky #9, Pittsburgh and Upper Freeport seams. The ROM coals were stored under three conditions - in ambient air, mine site tap water and dry nitrogen. Portions of these samples were also milled and processed (mineral matter removed), and these were then analyzed. These samples will serve as reference samples for an ongoing aging experiment to be described in later papers.

EXPERIMENTAL

Raw, milled and processed coals were received under N_2 in sealed bottles from Otisca Industries, Ltd. Raw coals were analyzed as received. Milled and processed coals had to be vacuum dried to remove water and water/pentane respectively. All samples were stored under dry N_2 when received.

Vacuum drying was done on a glass vacuum line. Samples were manipulated under dry N_2 when loaded in vacuum tubes and when the dried coal was removed from the vacuum tube. A liquid nitrogen trap was used to prevent pump oil from backstreaming onto the samples. Samples were evacuated at room temperature for five hours. After vacuum drying all three types of samples were treated the same for sample preparations. Air exposure has been minimized to less than two minutes for the transfer of samples into instruments.

ESCA spectra were recorded on Physical Electronics Model 5100 with a $Mg K_{\alpha 1,2}$ X-ray source (1253.6 eV). Experimental conditions of the X-ray were 300 W, 15 kV and 20 mA. Base pressure of the instrument was 2×10^{-9} torr and operating pressure ranged from 1×10^{-7} to 2×10^{-8} torr depending on the sample. The pass energy was 35 eV for high resolution narrow scans. All spectra were taken using a 45° take-off angle. The sampling depth at this take-off angle was approximately 60 Å.

For ESCA analysis sample preparation was accomplished by pressing coal powder onto double-sided sticky tape on a sample stage. The coal was transferred immediately to the introduction chamber of the instrument and pumped down for one hour before being moved into the main chamber for analysis. Wide scan spectra were taken for 15 - 20 minutes, followed by high resolution narrow region scans for a total of 50 minutes. There was no evidence of sample damage after 65 - 70 minutes under the X-ray.

Infrared spectra were acquired on two different FTIR systems. The first system was a Nicolet 7199A FTIR Spectrometer with an MTE detector. The bench was purged with dry air. Spectra were taken with 1000 scans. The second instrument was a Mattson Alpha Centauri with a DTGS detector. The bench was purged with dry N_2 . Spectra acquired were the result of 32 scans.

Samples for FTIR were prepared by KBr mull. Approximately .42g KBr was mixed with .006 - .01g of coal. The mull was pressed into a KBr pellet using a 13mm die under 8000 psi for 45 - 60 seconds.

RESULTS AND DISCUSSION

For this study, seven samples from each of the four seams were analyzed. In each sample set, three samples were raw coal (stored under air, N_2 or water), two were milled (air stored) and two were processed (stored under air and N_2). Tables 1 - 3 show surface atomic concentration results from ESCA analysis. Common to every one of these samples was the detection of C, O, and N. Sulfur was not detectable on the surface of three of the raw samples. Other elements found were Al, Si, Na, Fe and K. Na was found in both the Illinois #6 and Upper Freeport coals. Fe and K were only found in one of the Illinois raw samples.

Inorganic elements were detected in the greatest quantities in the raw samples. The percent surface atomic

concentrations decreased slightly after milling and decreased significantly after the coal was processed. In the processed samples, the inorganics were reduced to less than 1 % or, in many cases, were no longer detectable.

The storage conditions of the raw coals only showed a significant difference in the Illinois #6 and Upper Freeport coals. In the Kentucky #9 and Pittsburgh coals, the resultant % surface atomic concentrations were consistent through all three storage conditions. See Table 1. The two milled samples of Illinois #6 also showed inconsistency in the % surface atomic concentrations. For the other three coals, % surface atomic concentrations of the two milled samples were approximately equal. See Table 2. In the processed coals, the % surface atomic concentration of carbon was 85 - 88 % through all four coals. The % surface atomic concentration of oxygen was 10 - 12 %. Nitrogen remained consistent through all storage and processing steps, with a % surface atomic concentration of approximately 1 - 2 %. The % S remaining in the processed coals varied from .50 - 1.1 %. See Table 3.

In ESCA analysis, differential charging of the inorganic and organic species in the coals was noted. Standards consisting of mineral matter from each mine were run to determine the charge correcting for the inorganics. Si, Al, Na, K, Fe and inorganic S were corrected using Si (SiO_2), binding energy 103.4 eV. The organic species (C, O, N and organic S) were charge corrected using C 1s (hydrocarbon), binding energy 285.0 eV.

The C 1s region was curve fitted to five bands (3,4). See Table 4 and Figure 1. The initial band was set after standards of graphite were analyzed. This peak was at a binding energy of 284.6 eV. Oxidized coal was also analyzed to solidify the assignments of the carbon / oxygen species. Quantitation was done based on the curve fits. See Table 5. From raw to processed coal, a decrease is seen in the elemental / graphitic C and an increase in the aliphatic / aromatic C. C - O remained consistent, while C = O varied widely.

Sulfur has also been found to be present in inorganic and organic species. The inorganic sulfur is postulated to be sulfate compounds. In many samples, nitrogen appears as a broad peak at approximately 400 eV. Pyridine and pyrrole (5) appear at approximately 398.8 and 400.2 eV. It is postulated that both of these could be present.

Transmission FTIR spectra of all samples were collected. Correlations between FTIR and ESCA results support the observations of changing surface composition as raw coals went through processing. Peaks assigned to inorganics such as silicates vary in intensity proportional to the quantities found by ESCA. Similar correlations are found with the

organics.

CONCLUSIONS

ESCA and FTIR are useful methods in the analysis of coal surfaces. Composition and surface functionality can be elucidated. FTIR can be used to correlate these results deeper into the sample by transmission experiments.

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TABLE 1

	Illinois Raw			Kentucky Raw		
	Air	N	Water	Air	N	Water
C	43	23	33	71	69	71
O	40	51	48	21	22	22
N	1.1	.60	1.1	2.0	1.8	1.0
S	.30	---	---	1.1	1.2	1.2
Al	5.0	7.9	6.5	2.4	2.6	1.2
Si	9.2	15	11	3.2	3.5	2.8
Na	1.4	1.9	1.4	---	---	---
Fe	---	3.1	---	---	---	---
K	---	.89	---	---	---	---

TABLE 2

	Illinois		Pittsburgh	
	Milled			
C	54	66	72	72
O	35	27	22	22
N	1.5	1.5	1.5	1.5
S	.67	.45	.54	.62
Al	3.4	2.2	2.0	2.1
Si	5.9	4.4	3.3	3.5
Na	.50	.86	---	---

TABLE 3

	Illinois		Upper Freeport	
	Processed			
Air	85	85	86	88
N	12	12	9.7	9.4
	1.2	1.5	1.8	1.4
S	.72	1.1	.86	.52
Al	---	---	.74	---
Si	.92	.55	1.0	.44
Na	---	---	---	---

TABLE 4

I	284.2 eV	graphitic / elemental C
II	~ 285.0 eV	hydrocarbon (aliphatic or aromatic)
III	~ 286.6 eV	C - O
IV	~ 288.0 eV	C = O
V	~ 290.5 eV	COOH, carbonate or π to π^* shakeup

TABLE 5
% C Species by Curve Fitting

Illinois #6			
	Raw	Milled	Processed
I	13.85	2.61	2.43
II	58.22	67.27	70.70
III	19.24	17.25	18.26
IV	7.02	9.46	3.88
V	1.67	3.41	4.73

Figure 1

